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Systems and processes for providing hydrogen to fuel cells

Abstract:

A process and system for providing a hydrogen-containing gas stream to a fuel cell anode that includes providing a hydrogen-containing gas stream that includes carbon monoxide, introducing the hydrogen-containing gas stream into a pressure swing adsorption module that includes at least one carbon monoxide-selective adsorbent to produce a purified hydrogen-containing gas stream, and introducing the purified hydrogen-containing gas stream to the fuel cell anode. The pressure swing adsorption module can also include a second adsorbent and/or catalyst. Also disclosed is a fuel cell system coupled to an internal combustion engine and a fuel cell system that utilizes fuel cell waste heat for vaporizing a hydrocarbon/water mixture

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(71) Applicant (for all designated States except US): **QUESTAIR TECHNOLOGIES INC.** [CA/CA]; 6961 Russell Avenue, Burnaby, British Columbia V5J 4R8 (CA).

(72) Inventors; and

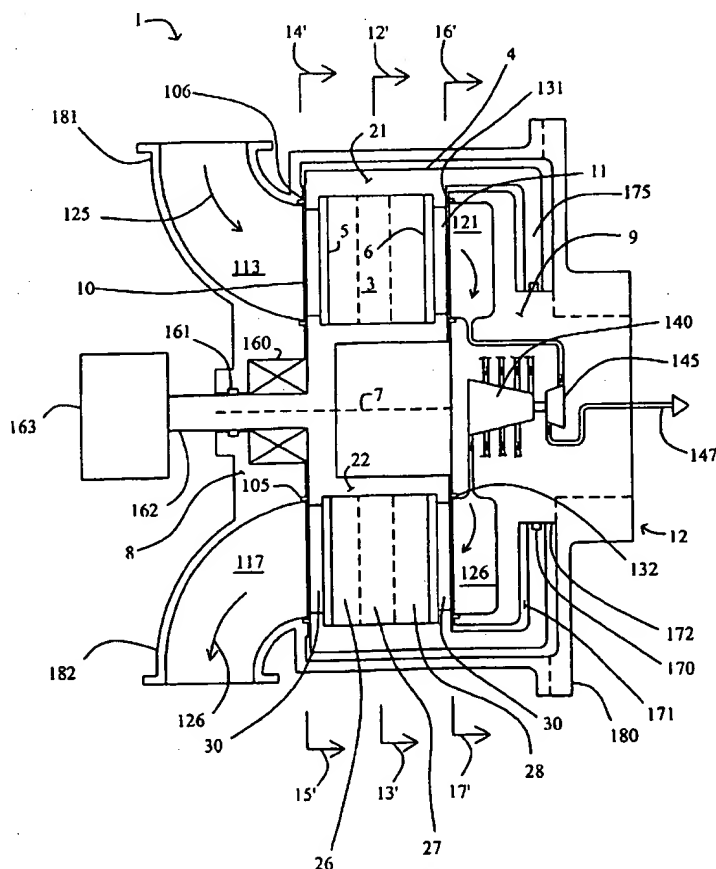
(75) Inventors/Applicants (for US only): **KEEFER, Bowie, G.** [CA/CA]; 4324 West 11th Avenue, Vancouver, British Columbia V6R 2M1 (CA). **SAWADA, James, A.** [CA/CA]; #225 - 1844 West 7th Avenue, Vancouver, British Columbia V6J 1S8 (CA). **JOHANNES, Erik, P.** [CA/CA]; #1605 - 7376 Halifax Street, Burnaby, British Columbia V5A 1M5 (CA). **ROY, Surajit** [CA/CA]; #210 - 6444 Willingdon Avenue, Burnaby, British Columbia V5H 2V6 (CA). **BROWN, Michael, J.** [CA/CA]; 1220 Nepal Crescent, West Vancouver, British Columbia V7T 2H3 (CA).

(74) Agent: **MCGRUDER, David, J.**; 480 - The Station, 601 West Cordova Street, Vancouver, British Columbia V6B 1G1 (CA).

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(54) Title: SYSTEMS AND PROCESSES FOR PROVIDING HYDROGEN TO FUEL CELLS



(57) Abstract: A process and system for providing a hydrogen-containing gas stream to a fuel cell anode that includes providing a hydrogen-containing gas stream that includes carbon monoxide, introducing the hydrogen-containing gas stream into a pressure swing adsorption module that includes at least one carbon monoxide-selective adsorbent to produce a purified hydrogen-containing gas stream, and introducing the purified hydrogen-containing gas stream to the fuel cell anode. The pressure swing adsorption module can also include a second adsorbent and/or catalyst. Also disclosed is a fuel cell system coupled to an internal combustion engine and a fuel cell system that utilizes fuel cell waste heat for vaporizing a hydrocarbon/water mixture.

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SYSTEMS AND PROCESSES FOR PROVIDING HYDROGEN TO FUEL CELLS

CROSS REFERENCE TO RELATED APPLICATIONS

5 This application claims the benefit of Canadian Patent Application No. 2,324,699, filed October 27, 2000, and Canadian Patent Application No. 2,324,702, filed October 27, 2000, the disclosures of which are incorporated herein by reference.

FIELD OF THE DISCLOSURE

10 The present disclosure relates to a fuel cell-based electrical generation system that enhances the efficiency and durability of the fuel cell.

BACKGROUND

15 Fuel cells provide an environmentally friendly source of electrical current. One form of fuel cell used for generating electrical power, particularly for vehicle propulsion and for smaller scale stationary power generation, includes an anode channel for receiving a flow of hydrogen gas, a cathode channel for receiving a flow of oxygen gas, and a polymer electrolyte membrane (PEM) which separates the anode channel from the cathode channel. Oxygen gas which enters the cathode, reacts with hydrogen ions, which cross the electrolyte to generate a flow of electrons.

20 Environmentally safe water vapor is produced as a byproduct.

 External production, purification, dispensing and storage of hydrogen (either as compressed gas or cryogenic liquid) requires costly infrastructure, while storing of hydrogen fuel on vehicles presents considerable technical and economic barriers. Accordingly, for stationary power generation, it is preferred to generate hydrogen from natural gas by steam reforming or partial oxidation followed
25 by water gas shift reaction. For fuel cell vehicles using a liquid fuel, it is preferred to generate hydrogen from methanol by steam reforming or from gasoline by partial oxidation or autothermal reforming, again followed by water gas shift reaction. However, the resulting hydrogen contains contaminants, such as carbon monoxide and carbon dioxide impurities, that cannot be tolerated respectively by the PEM fuel cell catalytic electrodes in more than trace levels.

30 The conventional method of removing residual carbon monoxide from the hydrogen feed to PEM fuel cells has been catalytic selective oxidation, which compromises efficiency as both the carbon monoxide and a fraction of the hydrogen are consumed by low temperature oxidation, without any recovery of the heat of combustion. Palladium diffusion membranes can be used for hydrogen purification, but have the disadvantages of delivering purified hydrogen at low pressure, and also the
35 use of rare and costly materials.

 Pressure swing adsorption systems (PSA) have the attractive features of being able to provide continuous sources of oxygen and hydrogen gas, without significant contaminant levels. PSA systems and vacuum pressure swing adsorption systems (VPSA) separate gas fractions from a gas

mixture by coordinating pressure cycling and flow reversals over an adsorber or adsorbent bed, which preferentially adsorbs a more readily adsorbed gas component relative to a less readily adsorbed gas component of the mixture. The total pressure of the gas mixture in the adsorber is elevated while the gas mixture is flowing through the adsorber from a first end to a second end thereof, and is reduced while the gas mixture is flowing through the adsorbent from the second end back to the first end. As the PSA cycle is repeated, the less readily adsorbed component is concentrated adjacent the second end of the adsorber, while the more readily adsorbed component is concentrated adjacent the first end of the adsorber. As a result, a "light" product (a gas fraction depleted in the more readily adsorbed component and enriched in the less readily adsorbed component) is delivered from the second end of the adsorber, and a "heavy" product (a gas fraction enriched in the more strongly adsorbed component) is exhausted from the first end of the adsorber.

Numerous copper-based, CO-selective adsorbents have been disclosed by Rabo et al (U.S. Patent No. 4,019,879), Hirai (U.S. Patent No. 4,587,114), Nishida et al. (U.S. Patent No. 4,743,276), Tajima et al. (U.S. Patent No. 4,783,433), Tsuji et al. (U.S. Patent No. 4,914,076), Xie et al. (U.S. Patent No. 4,917,711), Golden et al. (U.S. Patent Nos. 5,126,310; 5,258,571; and 5,531,809), and Hable et al. (U.S. Patent No. 6,060,032). Use of some such CO-selective adsorbents in pressure swing adsorption processes for removal or concentration of CO has been commercially established at industrial scale.

Using certain adsorbents for removing CO from reformat for PEM fuel cells has been investigated by researchers at the Argonne National Laboratory, as reported in the 1998 annual report of the Fuel Cells for Transportation Program of the U.S. Department of Energy, Office of Advanced Transportation Technologies. Bellows (U.S. Patent No. 5,604,047) discloses using selected noble metals, and the carbides and nitrides of certain metals, as carbon monoxide adsorbents in a steam displacement purge cycle for removing CO from reformat feed to fuel cells.

However, the conventional system for implementing pressure swing adsorption or vacuum pressure swing adsorption uses two or more stationary adsorbers in parallel, with directional valving at each end of each adsorber to connect the adsorbers in alternating sequence to pressure sources and sinks. This system is cumbersome and expensive to implement due to the large size of the adsorbers and the complexity of the valving required. Further, the conventional PSA system use of applied energy inefficiently because of irreversible gas expansion steps as adsorbers are cyclically pressurized and depressurized within the PSA process. Conventional PSA systems could not be applied to fuel cell power plants for vehicles, as such PSA systems are far too bulky and heavy because of their low cycle frequency and consequently large adsorbent inventory.

Another problem is the need for air compression with a substantial mechanical parasitic load to achieve high power density and high voltage efficiency with PEM fuel cells, either in the absence of PSA in prior art fuel cell systems, or to a lesser extent with the use of PSA to increase oxygen concentration. If, as usual by the case, mechanical power is provided by an electric motor powered by

the fuel cell, significant efficiency losses occur in electrical power conversion and conditioning for variable speed compressor drive, and the fuel cell stack must be substantially larger to support this parasitic load as well as the application load to which useful power is delivered. In prior art PEM fuel cell power plants for automotive and other transportation applications, approximately 20% of the gross power output of the fuel cell is diverted to the parasitic load of air compression.

Yet another problem arises in the need to provide heat for endothermic fuel processing reactions to generate low purity reformat hydrogen from hydrocarbon fuels (e.g. natural gas, gasoline or diesel fuel) or oxygenate fuels (e.g. methanol, ethanol or dimethyl ether). In the prior art, the necessary heat for steam reforming of natural gas or methanol is provided least in part by burning hydrogen provided as anode tail gas from the fuel cell. Especially in the case of methanol reforming, which can be performed at relatively low temperature, combustion of valuable hydrogen to generate such low grade heat is extremely detrimental to overall energetic efficiency.

Likewise, the necessary heat for processing heavier fuels, such as gasoline, is achieved by combusting a portion of the fuel in a partial oxidation or autothermal reforming process. Again, a portion of the high-grade fuel is consumed to upgrade the remainder of that fuel to low purity hydrogen than can be purified for use in the fuel cell. With a low temperature fuel cell, thermal efficiency of prior art fuel processing systems has been extremely low, as high grade fuel is consumed. No opportunity has been found for efficient thermal integration between a high temperature fuel processor and a low temperature fuel cell in transport applications.

Combined cycle power plants with a gas turbine cycle integrated with a fuel cell system have been disclosed. Fuel cell auxiliary power units have been proposed for automobiles and passenger railcars with internal combustion engines as primary power plants. PCT Patent Application Publication No. WO 00/16425 provides examples of how PSA units may be integrated with gas turbine power plants, or with fuel cell power plants having a gas turbine auxiliary engine.

SUMMARY OF THE DISCLOSURE

The disclosed fuel-cell-based electrical generation systems and processes address the deficiencies of the prior art fuel cell electrical generation systems. This is particularly true for purification of reformat hydrogen, energy-efficient PSA oxygen enrichment, heat recovery from the fuel cell stack and/or from combustion of hydrogen PSA tail gas, and thermal powering of air compression for the oxygen PSA and of any PSA vacuum pumping so as to minimize the size of the costly fuel cell stack while maximizing overall energetic efficiency of energy conversion from the raw fuel.

In general, the disclosed electrical current generating systems comprise a fuel cell, an oxygen gas delivery system, and a hydrogen gas delivery system. The fuel cell can include an anode channel having an anode gas inlet for receiving a supply of hydrogen gas, a cathode channel having a cathode gas inlet and a cathode gas outlet, and an electrolyte in communication with the anode and cathode channel for facilitating ion transport between the anode and cathode channel. The oxygen gas

delivery system is coupled to the cathode gas inlet and delivers air or oxygen (e.g. oxygen enriched air) to the cathode channel.

The oxygen gas delivery system may simply be an air blower. However, in certain embodiments it may incorporate an oxygen pressure swing adsorption system. For example, a rotary PSA system can be used comprising a rotary module having a stator and a rotor rotatable relative to the stator, for enriching oxygen gas from air. The rotor includes a number of flow paths for receiving adsorbent material therein for preferentially adsorbing a first gas component in response to increasing pressure in the flow paths relative to a second gas component. The pressure swing adsorption system also may include compression machinery coupled to the rotary module for facilitating gas flow through the flow paths for separating the first gas component from the second gas component. Described embodiments of the PSA system include a stator having a first stator valve surface, a second stator valve surface, and plurality of function compartments opening into the stator valve surfaces. The function compartments include a gas feed compartment, a light reflux exit compartment and a light reflux return compartment.

In one variation, the compression machinery comprises a compressor for delivering pressurized air to the gas feed compartment, and a light reflux expander positioned between and fluidly coupled to the light reflux exit compartment and the light reflux return compartment. A gas recirculating compressor is coupled to the light reflux expander for supplying oxygen gas, exhausted from the cathode gas outlet, under pressure to the cathode gas inlet. As a result, energy recovered from the pressure swing adsorption system can be applied to boost the pressure of oxygen gas delivered to the cathode gas inlet.

The oxygen gas delivery system is coupled to the cathode gas inlet and delivers oxygen gas to the cathode channel. The hydrogen gas delivery system supplies purified hydrogen gas to the anode gas inlet, and may recirculate hydrogen gas from the anode gas exit back to the anode gas inlet with increased purity so as to avoid accumulation of impurities in the anode channel.

In one variant of the above-described embodiments, the oxygen gas separation system comprises an oxygen pressure swing adsorption system, the hydrogen gas separation system comprises a reactor for producing a first hydrogen gas feed from hydrocarbon fuel, and a hydrogen pressure swing adsorption system is coupled to the reactor for purifying hydrogen gas received from the first hydrogen gas feed. Hydrogen gas from the anode exit may be recirculated to the hydrogen pressure swing adsorption system as a second hydrogen gas feed. Both pressure swing adsorption systems may include a rotary module having a stator and a rotor rotatable relative to the stator. The rotor includes a number of flow paths for receiving adsorbent material therein for preferentially adsorbing a first gas component in response to increasing pressure in the flow paths relative to a second gas component. The function compartments include a gas feed compartment and a heavy product compartment.

The feed gas to the hydrogen PSA system is reformat gas or syngas, generated in alternative

fuel processing methods known to the art by steam reforming (e.g. of methanol or natural gas or light hydrocarbons), or by autothermal reforming or partial oxidation ("POX") (e.g. of natural gas, gasoline or diesel fuel). The CO content of methanol reformat (generated by relatively low temperature steam reforming of methanol) is typically about 1% or somewhat less. Other fuel processors (e.g. steam
5 methane reformers, and POX or autothermal reformers operating on any feedstock) operate at a much higher temperature, and preferably include a lower temperature water gas shift reactor stage to reduce to CO content to about 1% or less.

The reformat gas contains hydrogen plus the basic impurity components of CO₂, CO and water vapor. If generated by air-blown POX or autothermal reforming, the reformat gas will also
10 contain a large inert fraction of nitrogen and argon. The fraction of inert atmospheric gases can be greatly reduced if an oxygen PSA system is used to supply the POX or autothermal reformer, either directly from the PSA, or as humid and still oxygen enriched air that has been passed through the fuel cell cathode channel, which was directly fed oxygen-enriched air from the PSA.

In one variation, the oxygen pressure swing adsorption system includes a compressor
15 coupled to the gas feed compartment for delivering pressurized air to the gas feed compartment, and a vacuum pump coupled to the compressor for extracting nitrogen product gas from the heavy product compartment. The hydrogen reactor comprises a steam reformer, including a burner, for producing syngas, and a water gas shift reactor coupled to the steam reformer for converting some CO to hydrogen. The hydrogen pressure swing adsorption system includes a vacuum pump for delivering
20 fuel gas from the heavy product compartment to the burner. The fuel gas is burned in the burner, and the heat generated therefrom is used to supply the endothermic heat of reaction necessary for the steam reformer reaction. The resulting reformat gas is delivered to the water gas shift reactor for removal of impurities, and then delivered as the impure hydrogen gas feed to the hydrogen pressure swing adsorption system.

25 In another variation, the invention includes a burner for burning fuel. The reactor comprises an autothermal reformer for producing syngas, and a water gas shift reactor coupled to the autothermal reformer for converting the syngas to the impure hydrogen gas feed. The compressor of the oxygen pressure swing adsorption system delivers pressurized air to the burner, and the heavy product gas is delivered from the hydrogen pressure swing adsorption system as tail gas to be burned
30 in the burner. The compression machine of the oxygen pressure swing adsorption system also includes an expander coupled to the compressor for driving the compressor from hot gas of combustion emitted from the burner. The feed compressor with the expander may be on a common shaft with a motor drive, or may constitute a free rotor similar to an automotive turbocharger. The same expander or another expander may be coupled to a vacuum pump to assist the PSA process.
35 Again, the vacuum pump with its expander may be provided as a free rotor similar to an automotive turbocharger. Heat from the burner may also be applied to preheat air and/or fuel supplied to the autothermal reformer.

Independently of whether PSA is used for oxygen enrichment, the disclosed processes and systems provide a hydrogen PSA apparatus for purifying the reformat. The hydrogen PSA may be designed to deliver high purity hydrogen, or else may be designed less stringently to achieve adequately high removal of noxious components or contaminants (harmful to the fuel cell) such as CO, H₂S, halogens, methanol, etc. In the latter case, the hydrogen PSA would in its first pass only achieve partial removal of less harmful constituents (e.g., N₂, Ar and CO₂). In that case, anode tail gas may be recycled to the feed end of the PSA inlet for use in a feed pressurization step, thus avoiding any need for mechanical recompression. Even when high hydrogen purity is specified for the PSA, this feature enables a small bleed from the end of the anode channel back to the feed pressurization step of the hydrogen PSA, as would be desirable for avoiding a strict dead-headed configuration with the risk of accumulation in the anode channel of any contaminant slip due to equipment imperfections or operational transient upsets.

Accordingly, a first embodiment of the disclosed processes and systems contemplates providing a hydrogen-containing gas stream that includes carbon monoxide, introducing the hydrogen-containing gas stream into a pressure swing adsorption module that includes at least one carbon monoxide-selective adsorbent to produce a purified hydrogen-containing gas stream, and introducing the purified hydrogen-containing gas stream to the fuel cell anode. A further disclosed process and system for providing a hydrogen-containing gas stream to a fuel cell anode involves introducing a hydrogen-containing feed gas stream into an adsorption module having at least a first adsorbent and at least one second material, and optionally plural materials selected from a second adsorbent, a steam reforming catalyst, and a water gas shift reaction catalyst, wherein the first adsorbent and the second adsorbent are chemically distinct and at least one of the first adsorbent or the second adsorbent preferentially adsorbs a contaminant in the hydrogen-containing feed gas stream to produce a purified hydrogen-containing gas stream.

Operating temperature of the adsorbers in the hydrogen PSA unit can be elevated well above ambient, as the reformat gas is supplied at a temperature after water gas shift of typically about 200°C, while operating temperatures of PEM fuel cells may extend from about 80°C to about 100°C. Alternatively, the adsorbers may be operated at a lower temperature if the reformat is cooled, thus providing an opportunity for partial removal of water and any methanol vapor by condensation before admission to the hydrogen PSA unit. Advantages of operation at moderately elevated temperature are (1) reformat coolers and water condensers upstream of the hydrogen PSA can be avoided, (2) PSA removal of water vapor and CO₂ may be more readily achieved at moderately elevated temperature compared to ambient temperature, (3) CO can be more selectively adsorbed than CO₂ over Cu(I)-loaded adsorbents, particularly at elevated temperature, and (4) kinetics of CO sorption and desorption on CO-selective sorbents may be greatly enhanced at higher temperature. Consequently, in certain embodiments the operating temperature range for the adsorbers is from about 80°C to about 200°C, and a more particular operating range is from about 100°C to about 160°C. As used herein,